REMOVAL OF VOLATILE ORGANIC COMPOUNDS FROM CONTAMINATED WATER USING AIR-SPARGED HYDROCYCLONE STRIPPING TECHNOLOGY

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The air-sparged hydrocyclone (ASH) technology offers the unique opportunity to achieve efficient removal of volatile organic compounds (VOCs) from contaminated water at a high specific capacity, more than 100 times that of conventional air stripping technologies. VOC stripping is the first application of the ASH as a contacting reactor rather than a flotation device. The effectiveness of the ASH system for this application has been demonstrated through a number of experiments. Results from these tests show that the ASH technology is very competitive with other stripping technologies and that single stage contaminant removal exceeding 90% can be achieved.

Zastosowanie hydrocyklonu napowietrzanego (ASH) do usuwania lotnych związków organicznych (VOC) z zanieczyszczonej wody umożliwia uzyskanie bardzo wysokiej efektywności, przy pojemności właściwej przekraczającej ponad 100-krotnie konwencjonalne technologie odpędzające. Odpędzanie VOC jest pierwszym przykładem zastosowania ASH jako kontaktora. Dotychczas ASH stosowany był jako urządzenie flotacyjne. Skuteczność ASH została udokumentowana podczas wielu eksperymentów, których rezultaty są bardzo konkurencyjne w stosunku do istniejacych systemów odpędzania. Wydajność usuwania zanieczyszczeń przekraczała 90% w jednostopniowym procesie oczyszczania.

Keywords: volatile organic compounds (VOC), air stripping, air-sparged hydrocyclone (ASH), contaminated water

1. INTRODUCTION

1.1. Volatile organic compounds

According to the definition used by World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) volatile organic compounds (VOCs) are substances which contain carbon atoms and which have a minimum vapor pressure of $1.3 \cdot 10^{-3}$ atm at standard temperature and pressure (293 K, 1 atm). They exclude CO, CO_2, organometallic compounds and organic acids.[1]

VOCs are increasingly regarded as posing unacceptable risks to humans and the environment. Two main health effects are associated with the exposure to VOCs: short-term effects such as headache, nausea, and eye irritation, and long-term effects such as cancer. In addition, two major indirect effects of VOCs on a global scale are reported to be ozone depletion, especially in the stratosphere above the Antarctic, and global climatic change due to the greenhouse effect.[1]

Halogenated hydrocarbons and other VOCs originating from industry and agriculture can be found in raw and finished drinking waters. These VOCs are usually introduced into water as by-products or waste streams from industrial, manufacturing or chemical production processes; some volatile chlorinated hydrocarbons are produced during chlorination processes. Another area of contamination with VOCs is groundwater, which can become polluted from leaking underground tanks, above-ground storage tank failures, surface chemical spills and waste disposal sites. Groundwater contamination in the U.S. is a critical environmental issue, since groundwater is the major source of drinking water for 50% of the urban population in the U.S. and 97% of the rural population. Furthermore, groundwater supplies one-fourth of all fresh water used in the United States and provides 40% of the water used for irrigation. In this regard, considerable efforts have been made in an attempt to reduce the release of VOCs, especially in the industrial countries where local levels and effects of VOCs are most pronounced.

1.2. Removal of volatile organic compounds from water

Volatilization of VOCs is a natural process for their elimination from water. This process is influenced by various factors which are directly connected with the physicochemical properties of the individual compounds, as well as the fluid mechanics of the air-water interface. Water solubility, vapor pressure, and the Henry's Law constant determine the rate of VOC evaporation.[1] Stripping of VOCs from water is another expression for their release by volatilisation. There are many VOC removal technologies which rely on the stripping process. The most common technologies are mechanical surface aeration, diffused aeration, spray or tray towers, open channel cascades, spray fountains, and countercurrent packed towers. Carbon adsorption and bioremediation are examples of processes based on other physicochemical phenomena for VOC elimination.

The principles of VOC transport between water and air phases for conventional stripping technologies are known.[2] Generally, the rate of mass transfer across an air-water interface is controlled by transport through the liquid film and can be expressed by the following equation:

$$\frac{1}{V}\frac{dm}{dt} = -K_L a(C_L^* - C_L) \qquad (1)$$

where: m=mass of solute (kg), V=liquid volume (m^3), t=time (s), K_L=overall mass transfer coefficient (m/s), a=specific interfacial area (m^2/m^3), C_L=bulk average concentration in the liquid phase (kg/m^3), and C_L^*=liquid concentration in equilibrium with the gas phase concentration C_G (kg/m^3).

For dilute solutions of nondissociating organic compounds in water, the value of C_L^* is approximately proportional to C_G, according to Henry's law for vapor-liquid partitioning

$$C_L^* = C_G/H_c \qquad (2)$$

in which H_c=Henry's constant (dimensionless) = ratio of the concentration in the gas phase to the concentration in the liquid phase at equilibrium.

Results reported in the literature[2-6] indicate that the greatest mass transfer of compounds from water to air is achieved for those compounds which have high Henry's Law constants and are relatively insoluble in water. It is impractical to attempt removing marginally volatile and highly soluble chemicals from water by stripping. Based on a review of the literature,[2-6] it is safe to say that when compound properties favor air stripping, maximum mass transfer will occur in air strippers that:

- maintain the greatest possible interfacial area between bulk liquid and uncontaminated air
- increase the magnitude of the liquid mass-transfer coefficient by providing sufficient turbulence to minimize the boundary layer thickness.

The air-sparged hydrocyclone technology is one of the new, emerging stripping technologies which can fulfill both requirements for maximum mass transfer.

1.3. Air-sparged hydrocyclone technology

The air-sparged hydrocyclone (ASH) technology was originally developed at the University of Utah for the fast and efficient flotation of fine particles from suspension.[7,8] The design of the high capacity ASH system was envisioned to establish a controlled high force field by swirl flow of slurry and to produce a high concentration of fine air bubbles with a directed motion to improve flotation separation efficiency.[9,10] Recent studies indicate that the fluid flow conditions inside the ASH system can be effectively exploited for the removal of VOCs from various industrial waste water streams by air stripping.

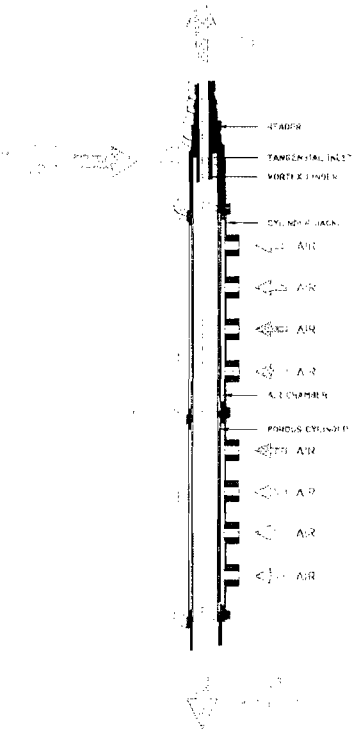

Figure 1. Schematic drawing of the air-sparged hydrocyclone.

A schematic drawing of the ASH unit is presented in Figure 1. The ASH unit consists of two concentric right-vertical tubes and a conventional cyclone header at the top. The porous inner tube is constructed of any suitable material such as plastic, ceramic, or stainless steel and allows for the sparging of air or any other gas or steam. The outer nonporous tube simply serves to establish an air jacket and provide for the even distribution of the air through the porous tube. Contaminated water is fed tangentially at the top through the cyclone header to develop a swirl flow adjacent to the inside surface of the porous tube, leaving an empty air core centered on the axis of the ASH unit. The high-velocity swirl flow shears the sparged air to produce a high concentration of small bubbles. As a result of the intimate interaction between these numerous fine bubbles and the contaminated water, VOCs in the water are stripped and transferred to the vapor phase, which is then transported radially to the center of the cyclone. The major portion of the vapor phase moves towards the vortex finder of the cyclone header, and is vented into an appropriate post-treatment device (activated carbon adsorption or thermal destruction units). Water stripped of its VOCs is discharged as an underflow product into a receiving tank. The specific capacity of the ASH system can reach 300-400 gallons per minute per cubic foot of cell volume, many times that of conventional air-stripping equipment.

The use of the ASH as a contacting reactor for VOC removal is the first non flotation application. Since this is a new field, a comparison has to be made between existing technologies and ASH stripping. The ASH equipment requires an operating space hundreds of times less than a packed tower or other aeration equipment, resulting in a significant savings in capital cost. The ASH can provide a unique opportunity for both high-capacity, fast separation of VOCs from large volume flows or a compact mobile system for small volume flows. In addition, due to its design features and the above-mentioned advantages, the ASH has the potential to perform VOC stripping directly from a particulate suspension containing up to 20% solids, an advantage not available with conventional technologies.

These attributes suggest that ASH-stripping should be competitive both technically and economically for the removal of VOCs from water, as indicated from a preliminary cost analysis presented in Table 1.

Table 1 Comparison of costs for packed tower and ASH for trichloroethylene removal (95% removal efficiency, feed 100 ppb, no solids in water).[11]

Capacity	Capital Cost [k$]		Yearly Power Cost [k$]		Yearly Maintenance Cost [k$]	
	Tower	ASH	Tower	ASH	Tower	ASH
20 gpm	56	8	0.29	0.69	29	2.7
100 gpm	77	19	0.90	3.40	31	9.5
700 gpm	160	62	5.70	12.0	45	22.4

2. EXPERIMENTAL

Experiments at the University of Utah pilot plant included preparation of aqueous solutions of the contaminants, stripping tests with a 2-inch diameter ASH unit, and analysis of influent and effluent streams using a gas chromatograph.

Three chemical compounds were used for the preparation solutions of trichloroethylene (TCE) (Mallinckrodt Chemical, 99.9%), acetone (Fisher Scientific, certified A.C.S.), and methanol (Fisher Scientific, certified A.C.S.). The main group of experiments was conducted with TCE solutions. The solutions were prepared in a 250L conditioning tank, the basic concentration ranging from 500 to 600 mg/L. In a few experiments, other concentrations were prepared to check the influence of this change on the stripping result. After 30 min of equilibration, the solutions were delivered to the ASH using a vertical sump pump GALIGHER 1.5SHA. Three water flowrates were selected: 35.0, 52.5, and 70.0 L/min, corresponding to inlet water pressures of 2.5, 5.0, and 10.0 psi, respectively.

The redesigned ASH-2C system was used for stripping experiments (see Figure 1). Two air delivery systems were used, one for low and one for high air flowrates. Air at low flowrates was provided using an air compressor and an arrangement of storage tanks, regulators, and valves which allowed for continuous regulation of the air flowrate between 0 and 250 L/min. Air was evenly distributed between the upper and lower sections of ASH (one air hose was connected to each ASH section, the other three air delivery connectors were closed). Air at high flowrates was provided by a ROOT DRESSER rotary air blower, model 32 URAI. This system allowed for five different air flowrates: 775, 1240, 1610, 2140, and 2280 L/min. All ASH air delivery connectors were utilized in this configuration.

Analysis of VOC concentrations in water was accomplished by gas chromatography (GC) with flame ionization detection (FID). All analyses were performed using a Hewlett Packard model 5890 Series II GC. A 30 m HP-5 (crosslinked 5% PH ME Silicone - 0.25 μm film thickness) capillary column (o.d. 0.32 mm) was used. A method of direct aqueous injection was selected,[12,13] and the following conditions were developed: helium carrier gas flowrate = 2 mL/min, sample volume = 1μL, temperature of the injection port = 150°C, initial oven temperature = 75°C, initial time = 0 min, rate = 30°C/min, final temperature = 180°C, final time = 5 min, detector temperature = 250°C. This method allowed for a detection limit of 3 mg/L of TCE, acetone, and methanol in water.

3. RESULTS AND DISCUSSION

The parameters which were changed during this investigation can be divided into three groups: (1) changes in the air flowrate, water flowrate, and the air to water flowrate ratio, (2) changes in the contaminant concentration, and (3) changes influencing Henry's constant, particularly temperature and contaminant type.

3.1. Water and air flowrates

The first group of experiments was performed using only TCE as the contaminant at ambient temperature (21 to 25°C). The influence of changes in the water and air flowrates on TCE removal is presented in Figure 2. These same results can be presented as a function of the air flowrate to water flowrate ratio (Q*). See Figure 3. During this investigation the Q* reached values as high as 70, which seem very high when compared to flotation applications of the ASH, where Q* rarely exceeds 5. Conversely, other stripping technologies operate at much higher values of Q*. For example, Q* in the range of 100 to 900 is typical for tray-type air strippers.[5]

The first point of significance from the data presented in Figures 2 and 3 is the systematic increase in the extent of TCE removal with increase in air flowrate. The general shape of these curves is as expected based on the steady state solution of the mass transfer equation.[16] See equation

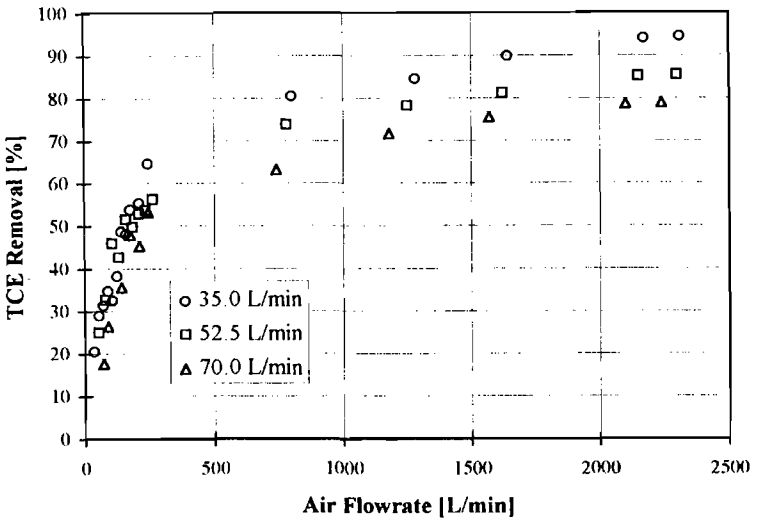

Figure 2. TCE removal efficiency for different water flowrates as a function of air flowrate. Insert: magnification of the lower portion of the scale.

5. Such behavior is expected because of an increase in the interfacial area for TCE transport to the gas phase. At low air flowrates this increase in interfacial area would be due to a decrease in bubble size and/or an increase in bubble concentration in the swirl layer hold-up volume. At high air flowrates only a gradual increase in TCE removal was observed with an increase in air flowrate, see Table 2. It seems that only a modest increase in interfacial area is achieved at high air flowrate. Future research will clarify this analysis. In this regard two air flowrate regimes can be identified, the one for air flowrates of less than approximately 250 L/min and the other for air flowrates above 250 L/min. As is evident from the data presented in Table 2, at low air flowrate the extent of removal of TCE is directly proportional to the air flowrate, whereas at high air flowrate the dependence is much less. When the air flowrate is doubled the extent of removal increases by 9.4 % from 80.5 % to 89.9 %.

Table 2. Examples of the TCE removal efficiency for low and high air flowrate (data for 35 L/min of water flowrate).

Low Air Flowrate		High Air Flowrate	
Air Flowrate [L/min]	TCE Removal [%]	Air Flowrate [L/min]	TCE Removal [%]
122.5	38.3	775	80.5
245.0	64.6	1610	89.9

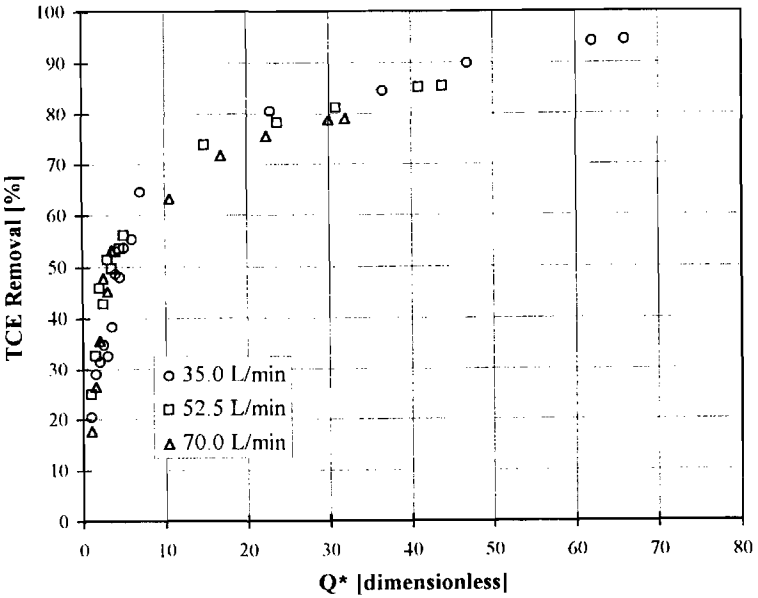

Figure 3 TCE removal efficiency for different air flowrates as a function of air flowrate to water flowrate ratio (Q*). Insert: magnification of the lower portion of the scale.

An expanded plot of the data for the low air flowrate regime is presented in the inserts for Figures 2 and 3. As mentioned previously at the low air flowrates, there is a substantial increase in the extent of TCE removal with an increase in the air flowrate. The influence of the water flowrate is not so significant at low air flowrates. The small variation in the extent of TCE removal with water flowrate may be related to the variation in the swirl flow characteristics.[9,10]

The results for high air flowrates reveal a distinct dependence on water flowrate as shown in Figure 2. This difference can be explained taking into consideration the swirl layer, its thickness, and the residence time at different water flowrates. The only available data correlating residence time, swirl layer thickness and water flowrate were obtained at low water flowrates for an air-sparged hydrocyclone configuration which included a froth pedestal (the froth pedestal is a cylinder which constrains the underflow and creates an annular discharge). Miller and Kineberg[7] reported that the swirl thickness is approximately 0.1 of the radius of the ASH. This condition is established from both experiment and theory. For example, the calculated values of the swirl layer thickness using Taylor's equation are 0.103 R or 2.6 mm for a 51-mm tube and 0.08R or 4.1 mm for a 102-mm tube. Experimental results indicate a swirl layer thickness which varies from 1.9 to 3.1 mm for the 51-mm tube. Based on this data, the hold-up volume of water in the swirl layer at high air flowrates may be independent of the water flowrate and thus the residence time would be inversely proportional to the water flowrate. In view of

this effect and perhaps other effects related to bubble size, concentration, and air [illegible] layer, the results presented in Figure 2 may be explained. When the data is normalized and the removal is plotted versus the relative air flowrate, Q*, the data are superimposed as shown in Figure 3 and which results indicate the importance of the air/water flowrate ratio.

From visual observations (texture and angle of streamlines in the underflow discharge) it appears that there is a transition in the multiphase flow characteristics at approximately 250 L/min of air flowrate, which may account for the distinct difference in the extent of TCE removal for the different air flowrate regimes. For example preliminary examination indicates that the swirl layer begins to expand significantly at air flowrates exceeding 250 L/min. Most probably this change results in differences in the extent of VOC removal for regions of low and high air flowrates. Further research will clarify this point.

3.2. Contaminant concentration

The second group of experiments was performed similarly to the first, using only TCE solutions. The influence of changes in the TCE concentration on the removal efficiency was examined. As can be seen in Table 3, there is no change in the recovery values at different TCE concentrations entering the ASH unit. Based on these results, it can be concluded that stripping in the ASH is a first-order process, typical of other stripping techniques, as reported in the literature.

Table 3. Results of the TCE stripping using air-sparged hydrocyclone at different concentrations (water flowrate 70 L/min, temperature 25°C).

Air Flowrate [L/min]	Inlet Concentration **608.8 mg/L**		Inlet Concentration **416.8 mg/L**		Inlet Concentration **227.0 mg/L**	
	Outlet Conc. [mg/L]	TCE Removal [%]	Outlet Conc. [mg/L]	TCE Removal [%]	Outlet Conc. [mg/L]	TCE Removal [%]
775	224.0	**63.2**	155.5	**62.7**	79.9	**64.8**
1240	437.1	**72.0**	120.4	**71.1**	63.6	**71.8**
1610	148.5	**75.6**	99.6	**76.1**	56.3	**75.2**
2140	129.1	**78.8**	87.1	**79.1**	44.9	**80.2**
2280	127.8	**79.0**	83.4	**80.0**	46.8	**79.4**

3.3. Henry's constant

During the third phase of this investigation, the influence of a change in Henry's constant on the extent of contaminant removal was examined. Variations in H_c were accomplished by changes in temperature and contaminant type.

The dimensionless form of Henry's constant, H_c, was used in this investigation (see equation 2), and is related to the frequently used dimensional form, H, which is expressed in terms of pressure and molar concentration, by the following equation:[3]

$$H_c = H/RT \tag{3}$$

where: H=Henry's constant (atm·m^3/mol), R=universal gas constant (R=8.206·10^{-5} atm·m^3/mol·K), T=absolute temperature (K).

The temperature dependence of Henry's constant can be calculated for a particular chemical from a series of regression equations developed by Lincoff and Gossett.[14] The equation describing the behavior of TCE has the following form:

$$H = \exp(11.94 - 4929/T) \quad (4)$$

The ASH stripping experiments were performed for three types of contaminants (TCE, acetone, and methanol) and three temperatures (24, 45, and 60°C), which resulted in the variation of Henry's constant values over five orders of magnitude (see Table 4). Results obtained for such a wide range of Henry's constant are not commonly reported in the literature.

Table 4. Values for Henry's constants for TCE, acetone, and methanol at different temperatures, as used for the data presented in Figure 4.

Contaminant	Temperature [°C]	H [atm·m³/mol]	H_c* [dimensionless]
TCE	60	$5.76 \cdot 10^{-2}$**	2.098
TCE	45	$2.87 \cdot 10^{-2}$**	1.098
TCE	24	$9.59 \cdot 10^{-3}$**	0.393
Acetone	25	$3.97 \cdot 10^{-5}$ (15)	$1.623 \cdot 10^{-3}$
Methanol	25	$4.66 \cdot 10^{-6}$ (15)	$1.905 \cdot 10^{-4}$

* - calculated using equation 3
**- calculated using equation 4

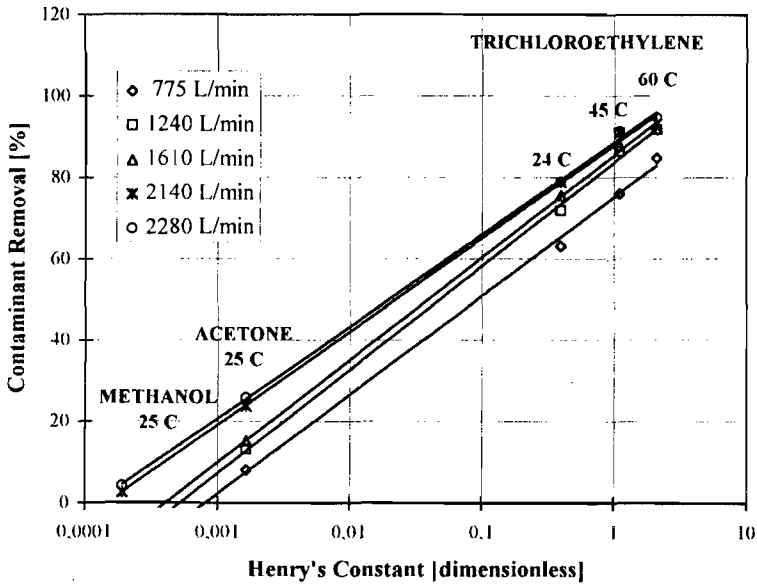

Figure 4. Contaminant removal efficiency for different air flowrates (water flowrate was constant - 70 L/min) as a function of Henry's constant.

The results of ASH stripping for different values of Henry's constant can be seen in Figure 4. The general increase in the extent of VOC removal with an increase in Henry's constant is as would be expected from theory and from previous studies. More significant is the excellent correlation of

Henry's constant with the extent of stripping. As can be seen, the results closely follow a logarithmic function for all operating conditions considered. The significance of this correlation can be examined only when the influence of other factors is known. The other factors can be found in the solution of the mass transfer equation (equation 1).[16] To determine the loss of a compound from the liquid phase, consider that the ASH behaves as a completely mixed flow reactor (CMFR). The steady state solution can be expressed in terms of the overall mass transfer coefficient relative to the liquid phase as follows:

$$\frac{C_{L,OUT}}{C_{L,FEED}} = [1+\frac{Q_G H_c}{Q_L}(1-\exp(-\frac{k_{f,L}(a)_R V_R}{Q_G H}))]^{-1} \quad (5)$$

where: Q_G=volumetric flowrate of gas, Q_L=volumetric flowrate of liquid, H_c=dimensionless Henry's constant, $k_{f,L}$=overall two-film mass transfer coefficient relative to the liquid-side concentration of a component, $(a)_R$=specific interfacial area per reactor volume, V_R=volume of liquid in the reactor

Equation 5 can be reorganized by the defining two dimensionless groups; the Stripping Factor, R_S:

$$R_S = \frac{Q_G H_c}{Q_L} = Q^* H_c \quad (6)$$

and the Stripping Parameter, β_S:

$$\beta_S = \frac{k_{f,L}(a)_R V_R}{Q_G H_c} \quad (7)$$

Thus the extent of removal can be expressed as:

$$Extent\ of\ Removal = 1-[1+Q^* H_c(1-\exp(-\beta))]^{-1}$$

In this solution to the mass transfer equation Henry's constant is not directly correlated with the extent of VOC removal, because it appears in both dimensionless groups. It is expected that future analysis will allow for a fundamental explanation of the empirical correlation between extent of removal and Henry's constant.

4. SUMMARY AND CONCLUSIONS

VOC removal from contaminated water by air stripping with the air-sparged hydrocyclone is the first such application of the ASH technology. The results obtained during this investigation demonstrate the applicability of the ASH technology in this field. Features such as short residence time, large interfacial area between water and air, and turbulent transport of air through the swirl layer give the ASH technology a distinct advantage over other stripping technologies, which are known for the poor economy of the aeration process resulting from the rapid saturation of air bubbles with VOCs.[2] Experimental results with respect to (1) changes in the air flowrate, water flowrate, and the air to water flowrate ratio, (2) changes in the contaminant concentration, and (3) changes influencing Henry's constant, particularly temperature and contaminant type have been given preliminary analysis in terms of the steady state solution to the traditional mass transfer equation.

Research described above is the first part of an investigation designed to establish detailed fundamental information which will provide the basis for application of the ASH technology to many recalcitrant remediation problems, such as emergency actions at remote locations and VOC or oxygen stripping on off-shore oil platforms.

5. ACKNOWLEDGMENTS

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